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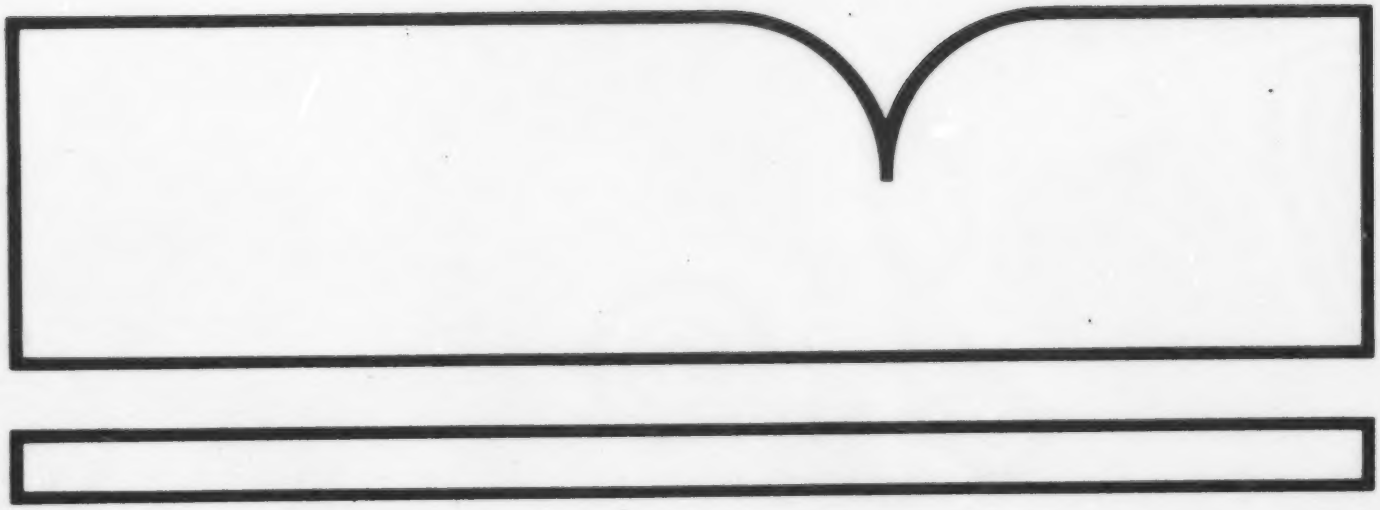

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MODELS AND STATISTICAL METHODS FOR GASEOUS EMISSION TESTING OF FINITE SOURCES IN WELL-MIXED CHAMBERS

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Abstract—Two families of mathematical models are proposed to represent either the concentration of a gaseous emission in or the accumulated amount exiting from a well-mixed, environmentally controlled test chamber. A thin film model, which seems applicable to such sources as carpet adhesive, etc., has the capability of isolating the true emission rate constant from chamber effects. It has successfully modeled emissions of methyl ethyl ketone, a C_8 alcohol, and butyl propionate from latex caulk. Chamber effects in the form of temporary wall retention were identified for the latter two compounds. An analogous, deep source, diffusion-limited model for plywood, etc., once fitted to a data set, can be used to generalize to other combinations of source surface area, chamber volume, and air exchange rate.

Key word index: Chamber testing, wall effects, volatile organic emissions, methyl ethyl ketone, butyl propionate, latex caulk, mathematical models, diffusion.

1. INTRODUCTION

A review of the current literature on controlled, chamber tests of gaseous emissions from indoor building materials suggests the lack of a precise definition of emission rate. Commonly, an estimate is reported which reflects average emission units per unit time over some sampling period. This, however, presumes the existence of a steady state condition, which appears to be an untenable assumption when the source is finite. Examples are testing outgassing from a swatch of plywood vs testing emissions from an unvented space heater. Hence, knowledgeable workers, such as Pickrell *et al.* (1984), report in addition the age of the source when the sample was obtained.

As an alternative, it is proposed that emission test results be described in terms of a mechanistic, time dependent family of models, indexed by one or more unknown constants which must be estimated from the data. Test results then are described in terms of emission rate constants within the context of the specified model rather than by average emission rates. Two such families of models are proposed here for the concentration of an emission in a well-mixed test chamber. The first seems appropriate for thin film sources such as carpet adhesive, varnishes, etc., while the second is more appropriate for deep sources such as particleboard, plywood, etc. where the length of the diffusion path may become limiting. In particular, results of such an analysis applied to emissions from a commercial latex caulking compound are presented.

2. THIN FILMS

2.1. *Model*

Consider the schematic,

$$\underset{A-x}{\text{FILM}} \underset{k_3}{\overset{k_1}{\rightleftharpoons}} \underset{x-y}{\text{CHAMBER}} \overset{k_2}{\rightarrow} \underset{y}{\text{TRAP}}$$

where A = initial amount of emittable substance in the source,
$x(t)$ = amount of substance emitted from the source to the chamber at time t,
$y(t)$ = amount of substance emitted from the chamber at time t,
$x(t) - y(t)$ = amount of substance in the chamber atmosphere at time t.

Assuming that the film is sufficiently thin so that all molecules of A have equal chance of being emitted, and that the air exchange rate is constant, then the system is described by the equations

$$\frac{d(A-x)}{dt} = -k_1(A-x)^{k_3/(k_3+1)} + k_3(x-y), \quad (1)$$

$$\frac{dy}{dt} = k_2(x-y),$$

equivalent to a reversible, two-stage reaction kinetics model. If V is the volume of the chamber and initial value conditions $x(0) = y(0) = 0$ hold, then the concentration of the substance in the exit flow, as

measured by an on-line analyzer, would be

$$C(t) = \frac{x(t) - y(t)}{V}, \tag{2}$$

while the amount of sample accumulated in the trap from time t_1 to time t_2 would be $I(t_1, t_2) = y(t_2) - y(t_1)$. In either case, an estimate of k_1 would seem to be the appropriate index of emission rate to be reported for that source and test condition. Since air flow rate is known independently, it seems best to assume the theoretical value of k_2 from the standard half-life formula, namely

$$k_2 = t_{1/2}^{-1} \ln 2, \tag{3}$$

where $t_{1/2}$ is the time required to make one complete air exchange, i.e. to give a 2:1 dilution of the contents of the chamber.

Due to the small amount of interface between a typical source and the chamber volume, the extent of true reversibility seems negligible. Hence, a non-zero k_3 is interpreted as a wall effect, i.e. the substance adheres to the equipment walls at a rate proportional to the chamber concentration and then bleeds off as the concentration drops.

Various solutions of Equation set (1) are given in Table 1. Model-1 reflects a solution for $k_3 = 0$ with k_4 a positive integer so that the rate of emission is proportional to a fractional power such as 1/2, 2/3, 3/4, etc. of the amount of substance remaining. In the limit, $k_4/(k_4 + 1) = 1$ as $k_4 \to \infty$ so that Model-2 with $k_3 \neq 0$ and Model-3 with $k_3 = 0$ result. There is a subtle but interesting distinction between Model-1 and Model-3. In the latter case, one expects the amount of substance in the source to decay exponentially. Zero is never attained, but only approached asyptotically. For Model-1, the decay rate is slower than exponential decay so long as $A - x \geq 1$, but then accelerates over exponential decay for $0 < A - x < 1$ and the source quickly goes to zero at $t = (k_4 + 1)A^{k_4/(k_4+1)}/k_1$.

Model-4, obtained by setting $k_4 = 0$, is thought to apply to a source whose emission rate is strictly surface-area limited, e.g. a cube of 1,4 dichlorobenzene. Model-4 is the only one of those presented which attains a non-zero, steady state chamber concentration of $k_1/[(k_2 + k_3)V]$.

2.2. *Analysis of latex caulk emissions*

Emission data for a commercially available, clear latex acrylic caulk (silicon based) are shown in Table 2. Initially, 5.05 g of caulk were spread over an area of 19 cm^2 on an aluminum plate. This swatch was sealed in a 166-ℓ, stainless test chamber which was maintained at 23°C, 50% relative humidity, and a constant air flow rate of 1.0 ℓ min^{-1}. A complete description of the test apparatus and test protocol is given by Sanchez *et al.* (1987). The air exchange rate is described by $t_{1/2} = 166/(60 \times 1.0) = 2.77$ h so that $k_2 = 0.25$ in hourly time units. Successive samples of the exiting air stream were passed through Tenax® traps, starting at the sampling initiation time shown and lasting through the indicated duration. The reported values of total volatile organics, methyl ethyl ketone, a C_8 alcohol, and

Table 1. Solutions to the thin film model: V = chamber volume, $C(t)$ = chamber concentration at time t, $I(t_1, t_2)$ = amount trapped at the chamber exit from times t_1 to t_2

Model-1: Emission rate proportional to $k_4/(k_4 + 1)$ power of amount remaining with $k_3 = 0$.
For $0 \leq t \leq (k_4 + 1)A^{1/(k_4+1)}/k_1$,

$$C(t) = A[1 - (1 - k_1 t/\{(k_4 + 1)A^{1/(k_4+1)}\})^{k_4+1}]/V - y/V,$$

$$y[t] = k_2 A \sum_{i=1}^{k_4+1} \frac{\Gamma(k_4 + 2)}{\Gamma(k_4 - i + 2)} \left[\frac{k_1}{(k_4 + 1)A^{1/(k_4+1)}}\right]^i \left\{\frac{e^{-k_2 t}}{k_2^{i+1}} - \sum_{j=0}^{i} \frac{t^{i-j}(-1)^{i+j}}{\Gamma(i - j + 1)k_2^{i+1}}\right\},$$

$$I(t_1, t_2) = k_2 A \sum_{i=1}^{k_4+1} \frac{\Gamma(k_4 + 2)}{\Gamma(k_4 - i + 2)} \left[\frac{k_1}{(k_4 + 1)A^{1/(k_4+1)}}\right]^i \left\{\frac{e^{-k_2 t_2} - e^{-k_2 t_1}}{k_2^{i+1}} - \sum_{j=0}^{i-1} \frac{(-1)^{i+j}(t_2^{i-j} - t_1^{i-j})}{\Gamma(i - j + 1)k_2^{i+1}}\right\}$$

while for $t > (k_4 + 1)A^{1/(k_4+1)}/k_1$,

$$C(t) = \{A - y[(k_4 + 1)A^{1/(k_4+1)}/k_1]\} \exp\{-k_2[t - (k_4 + 1)A^{1/(k_4+1)}/k_1]\}/V,$$

$$I(t_1, t_2) = \{A - y[(k_4 + 1)A^{1/(k_4+1)}/k_1]\} \exp[k_2(k_4 + 1)A^{1/(k_4+1)}/k_1](e^{-k_2 t_1} - e^{-k_2 t_2}).$$

Model-2: Emission rate proportional to amount remaining ($k_4 = \infty$) with $k_3 \neq 0$.

$$C(t) = k_1 A(e^{-r_2 t} - e^{-r_1 t})/[(r_1 - r_2)V],$$

$$I(t_1, t_2) = A\{r_1(e^{-r_2 t_1} - e^{-r_2 t_2}) - r_2(e^{-r_1 t_1} - e^{-r_1 t_2})\}/(r_1 - r_2),$$

where $r_1, r_2 = (k_1 + k_2 + k_3)/2 \pm \{(k_1 - k_2)^2 + k_3^2 + 2k_3(k_1 + k_2)\}^{1/2}/2$.

Model-3: Emission rate proportional to amount remaining ($k_4 = \infty$) with $k_3 = 0$.
Set $r_1 = k_1$ and $r_2 = k_2$ in Model-2.

Model-4: Emission rate constant ($k_4 = 0$) with $k_3 \neq 0$.

$$C(t) = k_1[1 - e^{-(k_2+k_3)t}]/[(k_2 + k_3)V] \quad \text{(until } A \text{ is exhausted)}$$

$$I(t_1, t_2) = k_1 k_2(t_2 - t_1)/(k_2 + k_3) - k_1 k_2\{e^{-(k_2+k_3)t_1} - e^{-(k_2+k_3)t_2}\}/(k_2 + k_3)^2.$$

Table 2. Observed emissions from 5.07 g of clear acrylic latex caulk (silicon based), tested at 23°C, 50% relative humidity, and 1.0 ℓ min^{-1} air flow rate in a 166-ℓ chamber

Obs.	Sampling initiation	Duration	Total organics	Methyl ethyl ketone	C_8 alcohol	Butyl propionate
	(Hours)	(Min)		(μg g^{-1})		
1	0.25	10	15.1	5.42	2.95	2.19
2	0.75	20	39.1	12.5	9.18	5.84
3	1.25	10	16.4	5.44	4.97	3.00
4	1.75	20	22.1	5.15	8.37	4.81
5	3.25	16.52	17.6	4.10	6.64	3.39
6	8.75	16.53	7.57	0.738	2.98	1.24
7	12.25	33.62	9.89	0.504	3.94	1.54
8	28.25	33.33	3.14	0.052	1.83	0.711
9	35.67	33.73	1.81	—	1.11	0.419
10	56.50	32.57	0.451	—	0.764	0.303
11	123.33	64.68	—	—	0.250	0.197
12	195.00	66.68	0.596	—	0.324	0.079

butyl propionate represent actual recovered amounts scaled up to represent the entire exiting air stream for each sampling duration. Since the data to be analyzed represented accumulations rather than concentrations, models defined by $I(t_1, t_2)$ rather than $C(t)$ were fitted.

All model fitting was accomplished by ordinary least squares using SAS® (1985) procedure NLIN. Estimated rate constants for Model-2 are given in Table 3. Also shown are estimates for a second sample of the same caulk, applied as 4.98 g to 19 cm^2 and tested under identical temperature and humidity conditions, but with an air flow rate of 5.11 ℓ min^{-1}. Nine samples were analyzed in this case covering a period of 71 h.

Model-2 invariably gave the best fit as reflected by the residual sum of squares. This is illustrated in Fig. 1 for butyl propionate measured at the lower air flow rate. For $k_4 = 1$ ($\frac{1}{2}$ power), Model-1 fitted the data through the first several hours of recovery, but then fell well below the recovered amounts after about 8 h. Estimates of A generally were slightly lower using this form of Model-1 compared to Model 2, but estimates of k_1 were usually an order of magnitude higher than those for Model-2. Model-1 with $k_4 = 2$ (2/3 power) was not able to account for the initial sudden rise in chamber concentration, so that still higher values of k_4 were not considered. For both methyl ethyl ketone data sets, $k_3 = 0$ was the best estimate so that, in effect,

Table 3. Thin film Model-2 rate constant estimates for emissions from latex caulk, tested at 23°C and 50% relative humidity

	Air exchange rate					
	1.0 ℓ min^{-1}			5.11 ℓ min^{-1}		
Emission	Estimate	Std. error	0.95 Conf. interval	Estimate	Std. error	0.95 Conf. interval
Total organics						
A(μg g^{-1})	692	97.4	467–917	441	56.9	301–580
k_1	4.17	2.93	0–10.9	3.73	1.60	0–7.64
k_3	2.05	1.89	0–6.41	1.68	2.11	0–6.86
$t_{C/2}$(h)	3.02			0.84		
Methyl ethyl ketone						
A(μg g^{-1})	151	43.4	39.1–263	113	14.3	78.6–148
k_1	8.39	13.9	0–44.1	7.00	3.99	0–16.8
k_3	0	3.22	0–8.27	0	2.08	0–5.09
$t_{C/2}$(h)	2.89			0.70		
C_8 alcohol						
A(μg g^{-1})	280	22.7	229–331	169	34.6	84.7–254
k_1	1.30	0.36	0.48–2.12	2.39	2.58	0–8.70
k_3	1.47	0.56	0.19–2.75	4.30	6.54	0–20.3
$t_{C/2}$(h)	3.61			0.99		
Butyl propionate						
A(μg g^{-1})	124	8.99	104–145	83.0	13.2	50.9–115
k_1	2.44	0.62	1.03–3.84	3.13	1.83	0–7.61
k_3	1.31	0.51	0.16–2.46	2.52	2.95	0–9.73
$t_{C/2}$(h)	3.21			0.89		

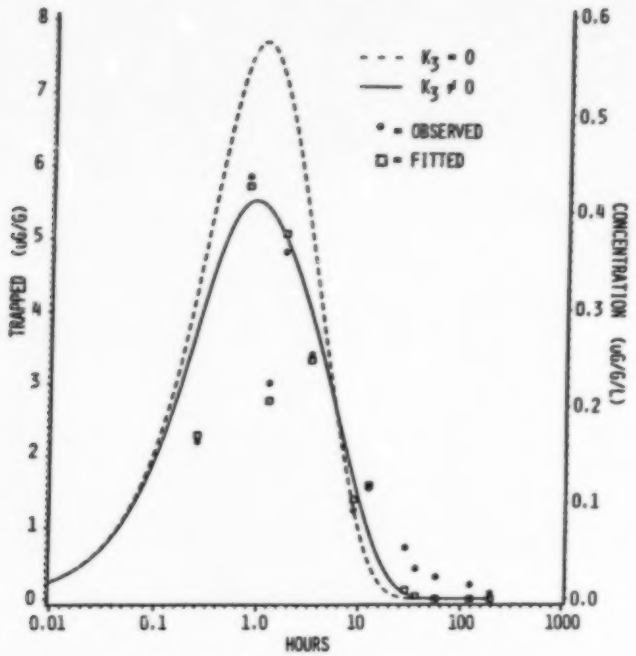


Fig. 1. Observed and fitted trapped amounts and estimated chamber concentrations with and without wall effects for butyl propionate emitted from latex caulk when tested at 23°C, 50% relative humidity, and an air flow rate of 1.0 ℓ min^{-1} in a 166-ℓ stainless steel chamber. Asterisks (*) represent the trapped amounts and boxes (□) are the corresponding fitted values.

even though Model-2 was fitted, Model-3 was implied by the data. Model-4 clearly did not apply because the trapped amounts continually decayed after the initial surge of concentration.

2.3. *Implications of the latex caulk analysis*

For two cases in Table 3, estimates of k_3 are significantly different from zero even for these small sample sizes, as reflected by the 0.95 confidence intervals. With the exception of both methyl ethyl ketone determinations, the remaining estimates of k_3 are considerably greater than zero. Since actual reversibility seems improbable, this provides strong evidence that at least some fraction of the heavier components was being stored temporarily on the chamber and conduit walls, and then being drained off as the chamber concentration decreased. Methyl ethyl ketone, being highly volatile, would not be expected to exhibit this behavior. The k_3 estimates are larger in both cases for the C_8 alcohol than for the butyl propionate, probably because the former was readily absorbed by a thin film of moisture on the interior walls.

In order to illustrate the significance of this effect, Fig. 1 shows a solid curve representing chamber concentration for butyl propionate, using estimates obtained at 1.0 ℓ min^{-1} air flow, and evaluated using the $C(t)$ equation corresponding to Model-2. By contrast, setting $k_3 = 0$ so that $C(t)$ corresponded to Model-3 resulted in the dashed line curve which represents what would have happened to the chamber concentration in the absence of wall effects. Presumably it is the latter result which should be reported to describe the emission characteristics of this particular latex caulk under the specified conditions. A different test chamber would likely have different wall characteristics and thus yield a different k_3, even though this had no bearing on the caulk emissions.

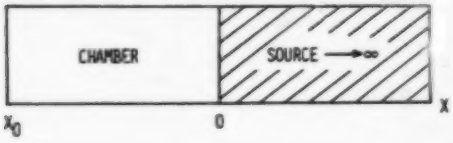
First half-lives, shown as $t_{C/2}$ in Table 3, represent the estimated time required to remove one-half the initial source from the chamber, in the absence of wall effects. These are estimated as the solution of $k_1 \exp(-k_2 t_{C/2}) - k_2 \exp(-k_1 t_{C/2}) = (k_1 - k_2)/2$. Since removal is not strictly by exponential decay, they are not true half-lives in the sense that the additional time required to remove one-half the remaining amount would be somewhat less than that reported in Table 3. The actual half-life of the source within the chamber, with $k_3 = 0$, can be estimated as $t_{S/2} = k_1^{-1} \ln 2$, e.g. $t_{S/2} = 0.284$ h for the butyl propionate at the lower air flow rate, compared to $t_{C/2} = 3.21$ h.

Finally, the variation in the estimates of A between the two air flow rates is a concern. Estimates invariably were lower at the high flow rate. Whether more of the solvents were trapped in the caulk matrix because of a more rapid filming over of the surface under these

conditions could not be determined. Alternatively, this may be a response to some unknown air flow rate by wall effect interaction.

3. DEEP SOURCE MODEL

Consider the following cross-sectional schematic of the test chamber:



Let $U(x, t)$ denote the concentration of the substance of interest at location x a. any time t. Now suppose that movement within the source is controlled by Fick's Law,

$$U_t(x, t) = -kU_{xx}(x, t), \quad (x > 0, t > 0) \qquad (4)$$

where k is the diffusion coefficient and the source is assumed to be semi-infinite in length. However, due to fan-mixing, the concentration within the chamber is uniform so that

$$U(x, t) = C(t), \quad (x_0 \leqslant x < 0, t > 0)$$

where x_0 reflects the finite dimensions of the chamber. If the concentration of the exiting gas will be measured, our problem is to determine the functional form of $C(t)$. Since flux of the substance through the face of the source per unit area per unit time is given by $kU_x(+0, t)$ and the removal rate, subject to a constant air flow rate, is proportional to the concentration, it is proposed that

$$\frac{dC}{dt} = kAU_x(+0,t)/V - k_2C, \qquad (5)$$

where A is the surface area of the source and V is the volume of the chamber.

Initial value conditions are

$$U(x,0) = C(0) = 0, \quad (x_0 \leqslant x < 0) \qquad (6)$$

since the chamber starts out free of the outgassed substance, and

$$U(x,0) = U_0, \quad (x \geqslant 0) \qquad (7)$$

assuming an initial uniform concentration in the source.

For boundary conditions, assume that the standard linear law of evaporation applies at the interface so that

$$kU_x(+0,t) = E\{U(+0,t) - C(t)\}, \qquad (8)$$

where $E > 0$ is a coefficient of transfer of the substance into the adjacent chamber, i.e. an evaporation constant. Physically, this condition states that the flux is proportional to the difference in concentrations between the surface of the source and the surrounding medium. Mathematically, $U_x(+0, t)$ is the slope of the concentration curve at the surface of the source at any time t.

A second boundary condition,

$$U_{xx}(+0,t) = -k_3e^{-k_4t} \quad (k_3, k_4 > 0) \qquad (9)$$

was obtained by consideration of the first term approximation to the general series solution of Equation (4), namely

$$U(x,t) \simeq A\cos(\lambda x/\sqrt{k}) + B\sin(\lambda x/\sqrt{k})\, e^{-\lambda^2 t}, \quad (x \geqslant 0). \qquad (10)$$

Then $U(+0,0) = U_0 \simeq A > 0$ provided $A > 0$, so that Equation (9) is consistent with the derived condition

$$U_{xx}(+0,t) \simeq -\lambda^2 Ae^{-\lambda^2 t}/k$$

obtained by differentiation of Equation (10). Mathematically, this represents an assumption that the concentration curve is concave downward everywhere to the right of the interface, but linearizes at an exponential rate as time proceeds.

Based on these assumptions and using standard methods, the solution of Equation (4) results in the model for chamber concentration at time t,

$$C(t) = a(1 - e^{-dt}) + b(e^{-ct} - e^{-dt}), \qquad (11)$$

where
$$a = (AE/V)(U_0 - kk_3/k_4)/(k_2 + AE/V), \qquad (12)$$
$$b = kk_3(AE/V)/(k_4(k_2 + AE/V - k_4)),$$
$$c = k_4,$$
$$d = k_2 + AE/V.$$

If the model defined by Equation (11) were fitted to concentration data, then the logical emission constants to report for this source would appear to be

$$E = (d - k_2)V/A,$$
$$k_4 = c$$
$$U_0 - kk_3/k_4 = ad/(d - k_2),$$
$$kk_3 = bc(d - c)/(d - k_2),$$

where again, it is presumed that the air exchange rate is known so that k_2 can be obtained from Equation (3). For if these were available from one set of test conditions, then combining these estimates with new values of A/V and $t_{1/2}$ (as expressed by k_2) in the formulae for a–d should allow one to predict emission concentrations for the second combination of loading ratio and air exchange rate by use of Equation (11), all without retesting. This is perhaps the most remarkable implication of the model.

The richness of this family of models is illustrated in Fig. 2 where chamber concentration is plotted on time for $t_{1/2} = 15$, 30, 60 and 120 min, with $A/V = 0.1$, $E = 0.3$, $k_4 = 0.04$, $U_0 - kk_3/k_4 = 3$, and $kk_3 = 0.1$. Technically, the model is non-physical for a finite source in that a steady-state concentration equal to the constant a defined by Equation (12) is attained when

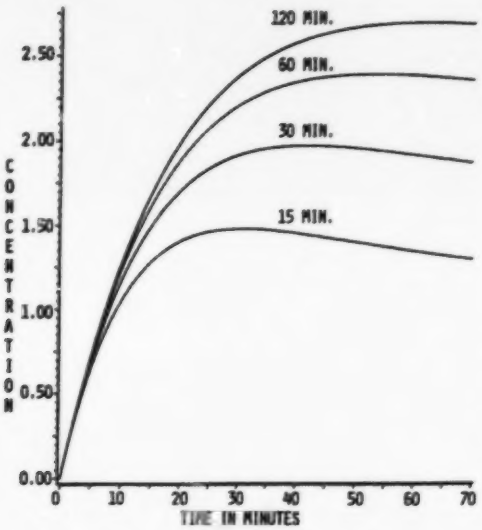


Fig. 2. Theoretical chamber concentrations for a diffusion-limited source when modeled with parameter settings $E = 0.3$, $k_4 = 0.04$, $kk_3 = 0.1$, $U_0 - kk_3/k_4 = 3$, $A/V = 0.1$, and one air exchange requiring 15, 30, 60 or 120 min.

the average length of the diffusion paths through the assumed infinitely thick source balances the air exchange rate. However, it may have practical value in modeling since the time required for say, a formaldehyde molecule to diffuse through half-inch plywood may be extremely large. For example, steady-state values corresponding to the 15-min curve in Fig. 2 are 0.0069 if the rate constants are expressed in units of minutes, or 0.25 if they are expressed in hourly units. Note from Equation (12) that since $k_2 = t_{1/2}^{-1} \ln 2$, the implied steady-state concentration is lower for a low air exchange rate than for a high rate. This may be explained by a consideration of the average length of the diffusion paths in either case when steady-state is attained.

The amount of sample accumulated in a trap from time t_1 to time t_2 is given by integration of Equation (11), namely

$$I(t_1,t_2) = a(t_2 - t_1) - b(e^{-ct_2} - e^{-ct_1})/c + (a+b)(e^{-dt_2} - e^{-dt_1})/d, \qquad (13)$$

where a–d are as previously defined. Hence, Equation (13) may provide a useful model for data reduction when samples are composited over time.

4. SUMMARY

The foregoing models have been developed assuming pure sources. However in most applications, the gaseous emission will consist of a mixture of compounds with a variety of vapor pressures. Suppose that v represents either the number of compounds or the number of classes of compounds with similar vapor pressures, and that $C_h(t)$ and $I_h(t_1,t_2)$ represent the concentration and sample accumulation for the h'th component ($h = 1, \ldots, v$). Then

$$C(t) = \sum_{h=1}^{v} C_h(t),$$

$$I(t_1,t_2) = \sum_{h=1}^{v} I_h(t_1,t_2)$$

provide composite models for either the concentration or accumulation of the mixture.

Since in this area of research, very few emissions of interest will lend themselves to direct, continuous-flow assessment of concentration, this author has felt compelled to develop models for the actual data, namely that which represents trapped accumulations, with an implied concentration model in the background. By allowing a pseudo-reversible path for a class of thin film models, the emissions phenomenon has been isolated from the characteristics of the individual test apparatus. This seems a useful result in that the test chamber results then can be combined by means of the models developed here with the absorption/adsorption characteristics of various, actual room environments.

The deep source, diffusion-limited model is still under development. The assumption of an infinitely thick source, leading to a non-zero, steady-state chamber concentration needs to be tested empirically. If in practical terms, it is a fair representation of reality, then it has the exciting possibility of being able to generalize test results at one surface area to chamber volume ratio (A/V) and air exchange rate ($t_{1/2}$) to any other combination of these three factors, without retesting. In light of the latex caulk results, perhaps the most immediate modification required should be to introduce a pseudo-reversible term into the model in order to isolate the true emission rate constants from the chamber effect.

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